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PLASMA CHEMISTRY FOR INORGANIC MATERIALS

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1. Introduction

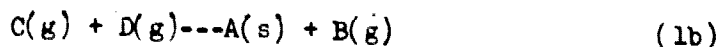
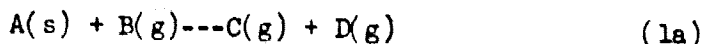
In recent years many research results have reported on, not /49*
only the distinctive feature that plasma has in gas phase reactions,
but also on its usefulness in practical applications to the reac-
tions of gas phases and solid phases, as well as the separating re-
action of solid phases from gas phases. Plasma that is used in chem-
ical reactions is generally divided into low temperature and warm
plasma. Each distinctive feature has been researched and plasma has
been practically applied to various inorganic compounds. Types of
plasma are in the manufacturing stage. Prior to manufacturing, in-
dustry adopted and introduced many results of research.

2. Plasma at Low Temperature and Inorganic Materials [1]

When inorganic materials are synthesized from plasma, it is
mainly necessary to consider the reaction in which plasma and solid
bodies participate. Reactions in which plasma at a low temperature
and solid bodies participate have two general classifications.

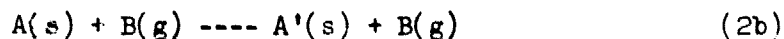
1) Chemical evaporation and chemical separation of solid bodies:

Plasma at low heat is used in chemical evaporation, as shown in
(1a), and chemical separation, as shown in (1b) (CVD [Chemical Vapor
Deposition])



* Numbers in the margin indicate pagination in the foreign text.

2) Surface modification of solid bodies, such as the oxidation and nitrification of solid bodies: surface oxidation, nitrification, etc. of solid bodies is shown in (2a) and the chemical reaction of the surface of a solid body in the surface modification of plastics is shown in (2b).



The material which exists in plasma at a low temperature is in an excited state when chemical reactions (1) and (2), which are shown above, are carried out. The same is true when the plasma is at a high temperature. The reactions can occur at a rather low temperature. Consequently, plasma is suitable for the composition and treatment of materials that are easily damaged by heat.

2.1 Surface Nitrification and Oxidation of Metals

Surface oxidation when using plasma for surface treatment of metals is researched for metal surface nitrification and oxide capsule formation of dielectric bodies, which aim mainly at case hardening of metals.

Case hardening of iron by direct glow discharge is a step in the use of what is called ion nitrification in surface nitrification of metals [2] This method turns nitrogen or nitrogen-hydrogen gas into plasma by direct glow discharge with a pressure lower by several torr. In the cathode drop, gas particles activate kinetic energy by a pronounced voltage drop and from this we have the method where iron, which was treated as a cathode, is nitrified. From the test results we can ascertain the formation of white chemical compound strata at the metal surface, which measure more than 10 μm thick. This chemical compound is identified as $\gamma\text{-Fe}_4\text{N}$ or $\epsilon\text{-Fe}_{2-3}\text{N}$. The case hardness of iron that has been nitrified becomes 2 times more than that of iron which has not been nitrified.

Zirconium and titanium have also been nitrified by the same ion nitrification method [3]. When nitrogen-hydrogen gas is made into plasma and titanium and zirconium are treated as cathodes, we can verify the formation of TiN and ZrN on the metal surface. We use a high frequency electrical discharge to turn nitrogen and nitrogen-hydrogen gases into plasma. Titanium, zirconium, and iron, which were placed in the plasma, were then nitrified [4-6].

This time, when we used the inductive coupling formula and /50 supplied high frequency to the gas, the conversion of gas into plasma and metal heating were carried out at the same time. In the surface of the metal, each nitride of the metal formed at a thickness of more than 10 μm . The hardness of the metal surface that was nitrified reached more than $1,500 \text{ kg/mm}^2$ for titanium and zirconium and more than $1,100 \text{ kg/mm}^2$ for iron.

The method, which used plasma in the formation of oxide capsules on the metal surface, is called plasma oxidation and in recent years we have noticed the usefulness of this method in the semiconductor industry [7]. Aluminum, tantalum and silicon were the metals that we nitrified using oxygen plasma. We developed oxygen plasma using microfrequency electric discharge. We placed the electrode vertically in the discharge tube. We put the silicon in the lower part of the top anode. We applied an exterior direct voltage of 10 V between both electrodes and caused a reaction between the O_2 ions, which were formed in the plasma, and the silicon. A thin layer of SiO_2 forms on the silicon surface. By this same method we also carried out the oxidation of Ga-As.

2.2 Plasma CVD

Plasma CVD is the reaction where the gaseous matter in low temperature plasma reacts and a new solid is formed on the substrate. A thin film of Si_3N_4 is formed prior to these steps [1].

From the use of plasma in CVD, it is possible that the substrate temperature stays at 500°C, compared with the existing exterior heating method. The substrate temperature is between 200° and 300°C.

In the high frequency glow discharge SiH_4 and N_2O supply a thin membrane of SiO_2 and SiH_4 . NH_3 forms a thin membrane of Si_3N_4 . In this method, high frequency is provided between two electrodes, which are parallel, and a glow discharge is produced. The method which separates the plasma origin and the separating substrate also varies in origin. In this development of plasma, the use of microfrequency is distinctive [8]. When we verify the N atom without witnessing direct discharge and high frequency discharge, microfrequency is used to turn nitrogen into plasma. This is efficient due to the CVD reaction. We also carry out the separation of the thin SiO_2 membrane by the reaction between SiCl_4 and oxygen plasma using microfrequency discharge [1]. A thin oxide membrane is obtained and shows a peculiarity making it promising as material used to conduct light waves.

SiH_4 separates at a high frequency glow discharge. The method in which noncrystalloid silicon is separated on top of the substrate, which is heated to between 200° and 300°C, has been reported. It has good prospects as a raw material for solar cell batteries.

TiCl_4 , H_2 and CH_4 are supplied in the argon plasma, which is produced by direct glow discharge, and the thin TiC membrane is coated with stainless steel, which is a cathode [9]. The thickness of TiC is 15 μm and the hardness is 2,900 kg/mm^2 . TiCl_4 is supplied in nitrogen-hydrogen plasma using high frequency discharge and gold colored TiN is separated in the iron substrate. The thickness of TiN is about 20 μm and the hardness of the surface is 2,600 kg/mm^2 .

Aluminum and titanium, which are placed in nitrogen-chlorine compound plasma that is produced from high frequency discharge, become chloride gases, and become nitrides when they react with nitrogen. We obtain single crystals of TiN and AlN from what is called plasma chemistry transmission.

2.3 Materials and Organization in Reactions Using Low Heat

In recent years research has been done on medium bodies in chemical reactions that used low heat plasma. The research was done by mass spectrometry and radiation spectroscopy. For example, an NH radical exists in nitrogen-hydrogen plasma with ion nitrification and high frequency discharge [2]. We have verified the presence of an N atom in nitrogen plasma, which is produced from microfrequency discharges [10]. And we have noted the separation of a chlorine atom, which is supplied in the plasma CVD [11]. It is thought that the existence of this radical and atom cause a drop in the substrate temperature, which is a unique reaction of low temperature plasma.

3. Warm Plasma and Inorganic Materials

Warm plasma is the heavy particles and electrons of atoms, ions, etc. that are in a state of thermal equilibrium. Therefore, the high energy of the heavy particles can be used as a heat source. If we use the plasma as a reaction source, there is the possibility that various new chemical reactions will occur because the ions and atoms /51 in plasma are in a high energy state. Moreover, in the plasma jet, the speed of the current of the plasma is 500 m/s and the current speed of the powder, which is supplied by the plasma, is 100 m/s. Therefore, the powder in the plasma has a high momentum. This high momentum can also be used in chemical reactions. The many chemical reactions at a high temperature are endothermic reactions. It is necessary to freeze the products by rapid cooling in order to collect the products at a normal temperature. This is accomplished with relative ease when we use plasma.

Practical research has been done on warm plasma and the formation of many inorganic materials. A brief explanation of the possibility of using plasma in the formation of these materials is presented below.

3.2 The Formation of Minute Oxide Particles [13]

Al_2O_3 and SiO_2 and their carbon compounds are rotated in a plasma furnace. The AlO and SiO , which are evaporated, react with water vapor and are hydrolyzed. Tiny particles of SiO_2 and Al_2O_3 are obtained. These tiny particles contain a small amount of moisture and show thixotropy.

3.3 The Composition of Oxides from Chloride Vapor

Oxygen plasma is used in the composition of oxides from oxygen decomposition of chlorides. High frequency induction plasma is used and TiO_2 powder, which is used in pure cosmetics, is obtained by oxygen decomposition of TiCl_4 . The sintered Al_2O_3 and $\text{Al}_2\text{O}_3\text{-SiO}_2$ powders of submicron order are obtained by oxygen decomposition of the chemical compounds of AlCl_3 and $\text{AlCl}_3\text{-SiCl}_4$.

SiCl_4 is placed in oxygen plasma. The SiO_2 that is formed is melted and made into crystals. We obtain quartz crystals. In obtaining the quartz crystal by this method, we use an oxyhydrogen flame. When compared with the other compounds we produced, quartz has a remarkably low hydrogen content, and is a material that can be used as fibers for light wave transmission.

3.4 The Composition of Carbides and Nitrides [15]

By decomposition of argon plasma of inorganic compounds of SiCH_3Cl_3 and $\text{Si}(\text{CH}_3)_2\text{Cl}_2$, a sintered β SiC powder with a diameter of 5,000 Angstroms is obtained. Minute particles of aluminum and silicon are found in argon-ammonia plasma, and minute, sintered particles of AlN , Si_3N_4 , etc. are obtained.

A nitride from the nitrification of metals is formed by nitrogen plasma using a plasma arc furnace. Various carbides are produced by

heating argon plasma of oxide and carbide compounds. We did carry out the production of the carbides and we have presented it here in an abridged form.

3.5 Freezing of High Temperature Phases by Plasma Arc Welding and Plasma Jet [17]

Because of the progress in improving heat and wear resistance of raw materials, raw materials with a high melting point have been plasma arc welded. The particles supplied in the plasma jet are melted and accelerated to reach the raw materials. An adherent insulation is formed. Plasma arc welding of the tungsten in a rocket engine nozzle can begin to be used. Plasma is used in the arc welding of oxides, carbides and nitrides.

The stable hexagonal compounds of $\eta\text{-MoC}_{1-x}$, WC, and TaN and the rhombohedron compound of Mo_2B_5 exist in the plasma jet at a normal temperature. When heat is added, cube shaped compounds of αMoC_{1-x} , βWC_{1-x} , and TaN_{1-x} and hexagonal shaped MoB_2 , which are stable at high temperatures, can be obtained.

4. The Use of Plasma in the Development of New Energy Materials

Developmental research has been carried out on various new energy substances that can be used as substitutes for petroleum. This research is progressing at a fast rate. We will show some examples of these substitutes where plasma chemistry is playing many roles in this research.

4.1 The Production of Silicon for Use in Solar Cell Batteries [18]

At the ERDA (Energy Research and Development Agency) in the United States, developmental research on various production methods

of silicon for solar cell batteries is being commissioned by many development agencies. The final target for production cost is \$10/kg of Si. This is still in the research phase, but the possibility of accomplishing this goal by using plasma is evident.

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At the Westinghouse Company, SiCl_4 and sodium are supplied and react in argon-hydrogen plasma. Research on the products of silicon is being carried out. Direct plasma contact is used and SiCl_4 and sodium are supplied in the form of liquids in the argon-hydrogen plasma that was produced. The sodium and SiCl_4 are evaporated and reactions are carried out in the gaseous phase. Silicon is separated in the reaction chamber. At this same company, a plasma arc heater is used (output is 1.6 MW). The production of silicon by the same reaction is planned. Two arc heaters are placed in the reaction chamber. The SiCl_4 and sodium, which are supplied in the plasma produced, react and the silicon is separated. According to the estimates of this company, the production cost of Si is \$9.42/kg [19].

4.2 Insulation of the Inner Surface of Furnace Walls in a Nuclear Fusion Reactor and Its Reaction [20]

The inner surface of furnace walls of the nuclear fusion reactor interfaces with the plasma. This results in particles and membranes being formed which are filtered from the plasma at a high temperature. Impurities are mixed in the plasma and radiation loss is increased. Consequently, the raw material of the walls requires a long chemical reaction with hydrogen plasma at a low Z (atom number). From these facts, there are good prospects for ceramics being made from raw material walls of SiC, TiC, Si_3N_4 and TiN. Because of this, the inorganic materials mentioned above are insulated by molybdenum and stainless steel.

Various methods have been tested for insulation of inorganic materials, as mentioned above. Among these, plasma CVD, surface nitrification of metals and plasma arc welding which were previously

introduced, are being promoted as prospective methods. It is thought that the role which plasma chemistry plays in the insulation of inorganic materials will grow.

5. Conclusion

We have outlined the practical application of plasma chemistry to the development of inorganic materials with both low temperature and warm plasma. We were not able to present detailed facts, so please refer to the references that follow.

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